

Reaction Kinetics of Carboxymethylation of Cornstarch

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ABSTRACT: Reaction kinetics of carboxymethylation of cornstarch in the reaction media of ethanol was studied in this article by determining the changes of NaOH concentration and degree of substitute of reacting matter in the reaction process at different temperature. The equation of reaction rate has been set up and proved to be corresponding with the second-order reaction. The main and

side reaction rate constants at different temperature and the main and the side reaction activation energy have been obtained, respectively. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 121: 1901–1907, 2011

Key words: reaction kinetics; carboxymethylation; cornstarch; reaction rate constant; activation energy

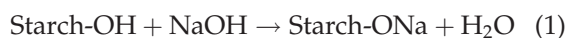
INTRODUCTION

As a natural, renewable, and environment friendly material, the modified starches are being used more and more widely in recent years. Among the various kinds of modified starches, carboxymethyl starch (CMS), which is anionic and soluble in cold water and has the functions of thickening, adhesion, water-absorption, film-formation and etc, is widely used in many industry areas such as sizing, printing, oil field, coating, food, and pharmaceutical industry etc. It is one of the most important starch ether derivatives. The studies about the preparation and the application of CMS are very activity.^{1–10} However there are few research papers concerning the reaction theory of the carboxymethylation of starch. The study about reaction kinetics of carboxymethylation of cornstarch was introduced in this article.

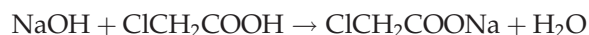
Elements about reaction kinetics of carboxymethylation of starch

The reaction of starch with monochloroacetic acid in the presence of alkali belongs to bimolecular nucleophilic substitution (SN₂). The reaction process is as follows^{2–6}

- a. First, sodium hydroxide reacting with starch to form alkaline starch, the reaction formula is as follows:



- b. Second, following chloroacetic acid added, it rapidly neutralizes the dissociated sodium hydroxide or alkaline starch and converts to sodium chloroacetate in the ethanol media. The reaction formula is:



or



Because NaOH is easy to combine with the starch, and chloroacetic acid has priority to neutralize the free NaOH in the media, thus assuming that the free NaOH does not exist and all the NaOH in the media joins with starch to form alkaline starch. Then the reaction formula of starch with sodium chloroacetate can be presented as:



And the side-reaction formula of the hydrolysis of sodium chloroacetate in the presence of alkaline can be described as follows



The reaction in Formula 3 and Formula 4 are parallel reactions. The overall reaction rate equation is followed.

$$-\frac{d[\text{ClCH}_2\text{COONa}]}{dt} = k[\text{ClCH}_2\text{COONa}][\text{St-ONa}] \quad (5)$$

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It is a reaction rate equation of second-order. As we have assumed all NaOH convert to St-ONa, and NaOH is equivalent to St-ONa in acid-base titration, so there is $[\text{NaOH}] = [\text{St-ONa}]$. Supposing the initial concentrations of sodium chloroacetate and alkaline starch are $[\text{ClCH}_2\text{COONa}]_0$ and $[\text{NaOH}]_0$, respectively, the reacted amount of $[\text{ClCH}_2\text{COONa}]$ or $[\text{NaOH}]$ is x at a certain reaction time t . Because of $[\text{ClCH}_2\text{COONa}]_0 \neq [\text{NaOH}]_0$, to integrate the reaction rate eq. (5), the following Formula 6 is obtained¹¹

$$\frac{1}{[\text{ClCH}_2\text{COONa}]_0 - [\text{NaOH}]_0} \times \ln \frac{[\text{NaOH}]_0([\text{ClCH}_2\text{COONa}]_0 - x)}{[\text{ClCH}_2\text{COONa}]_0([\text{NaOH}]_0 - x)} = kt \quad (6)$$

In eq. (6), k is the overall reaction rate constant. As the concentration of sodium hydroxide can be detected easily by acid-base titration to the sample during the reaction, the initial concentration of $[\text{NaOH}]_0$ and the reaction consumption of $[\text{NaOH}]$ (x) at certain time can be easily obtained. According to the reaction eqs. (3) and (4), the consumption of $\text{ClCH}_2\text{COONa}$ and NaOH are the same in molar amount, so the $[\text{ClCH}_2\text{COONa}]_0$ can be calculated by the added chloroacetic acid and the consumption of sodium hydroxide. A straight line is drawn according to the eq. (6). The slope of the straight line is the overall reaction rate constant k . According to the kinetics character of parallel reaction,¹² the ratio of reaction products concentration equals to the ratio of parallel reaction rate constant. Let k_1 and k_2 be the main and the side reaction rate constants, respectively. There is a relationship among the three reaction rate constants as follows:

$$k = k_1 + k_2 \quad (7)$$

$$\frac{k_1}{k_2} = \frac{\text{RE}}{1 - \text{RE}} \quad (8)$$

In eq. (8), RE is reaction efficiency or etherification efficiency. It can be obtained by the ratio of determined result of DS (degree of substitute) with the theoretical calculations of DS. According to the eqs. (7) and (8), k_1 and k_2 can be calculated from k and RE.

Moreover, based on Arrhenius equation, the main and side reaction activation energy can be calculated by reaction rate constants in different reaction temperatures.

Feasibility of the research method

The research about reaction kinetics of carboxymethylation of starch was carried out by determining

the changes of NaOH concentration and DS of reaction matter during the reaction process. The method was relatively simple, but there were many respects which may cause errors. Apart from analysis method itself and data processing, errors mainly come from some factors in experiment operation. One of the factors was sampling process. As the reactant was suspension, sampling may be uneven. Another factor was that the chemical analysis operation for determination of DS included complicated procedures—acidifying, washing, drying, weighing, resolving, and back-titrating, and meanwhile the sample was in large quantities, both of which may lead to errors in the result of DS. However, the results obtained were approximately matched with theory analysis; the equation of reaction rate was proved to correspond with the reaction of second-order. The main and side reaction rate constants at different temperatures were approximately matched with Arrhenius equation. So this experiment method was feasible.

EXPERIMENTAL

Materials

Corn starch contained $\sim 12.5\%$ water, provided by Yongchang (Henan, China). Food grade ethyl alcohol was obtained from Xinxiang Alcohol Factory (Henan, China). Monochloroacetic acid, purity 97%, obtained from Dongda Chemical (Henan, China). Sodium hydroxide, purity higher than 99%, made by Tianjin Chemical Plant (Tianjin, China).

0.1 mol L⁻¹ NaOH standard solution.

0.1 mol L⁻¹ HCl standard solution.

0.5 mol L⁻¹ HCl standard solution.

0.1% phenolp indicator.

0.1 mol L⁻¹ AgNO₃ standard solution.

Equipments

Electric mixer (Hangzhou Electric, China); Constant temperature water bath boiler.

Methods

Preparation

About 40 g starch was slurried in 100 mL ethyl alcohol in 250 mL three-necked round-bottomed reaction flask equipped with a PTFE-sealed stirrer and reflux condenser. About 4.5 g NaOH had been dissolved in 8 mL water previously and the solution was cooled for use (Note: keeping the volume ratio of alcohol and total water to be 84 : 16, the water inside the starch and inside the ethyl alcohol was included in the total water. The weight ratio of NaOH and ClCH_2COOH was kept at 0.9 : 1.0. As the over

TABLE I
The Experimental Data of Reaction Kinetics of Carboxymethylation of Starch (50°C)

No.	t (min)	V_{HCl} (mL)	M_{NaOH}	ΔM_{NaOH}	DS_{th}	DS	RE (%)
0			0.427			0	
1	0	8.0	0.401	0.027	0.0175	0.0163	
2	30	7.1	0.356	0.045	0.0292	0.0396	81.8
3	60	6.4	0.321	0.080	0.0518	0.0586	81.2
4	90	5.7	0.286	0.115	0.0745	0.0791	84.3
5	120	5.0	0.251	0.150	0.0972	0.0968	82.8
5	180	4.2	0.210	0.191	0.1238	0.1201	83.8
6	240	3.6	0.180	0.221	0.1437	0.1477	91.4

swelling of reactant with higher DS in later reaction stage may affect sampling homogeneity, the kinetic experiments were carried out in lower water ratio and lower DS range⁷). The solution of NaOH was added into flask. The slurry mixture was stirred for 30 min before the addition of the 5 g solid of monochloroacetic acid. Then after keeping stirring for 40 min at 30°C, timing and sampling was started as soon as it was raised to a scheduled reaction temperature. Sampling was kept repeating in every 30 or 60 min until the concentration of residue NaOH become too small or its variation was too low. The carboxymethylation temperature was set at 70, 60°C, 50°C, respectively.

Sampling operation

The operation of sampling was as follows: 10 mL reactant was sucked up from the flask by suction pipette and immediately poured into 50 mL 80% ethanol for diluting and cooling it to stop the reaction. Then the sample was titrated rapidly by 0.5mol L⁻¹ hydrochloric acid standard solution with phenolph indicator. The neutralized reaction product was filtrated and washed by 80% ethanol to free of chloride, and dried for determination of DS.

Analysis

DS of the CMS was determined according to the method of ISO 11216: 1998(E).¹³ the principle is as follows.

The carboxymethyl groups are converted into the acid form by acidifying a solution or a suspension of the starch with hydrochloric acid. After the starch is precipitated with methanol, it is allowed to settle before being filtered off on a sintered glass crucible. The excess acid is completely removed by washing with methanol. The starch is dried and a weighed portion is treated with a measured excess of sodium hydroxide solution. The sodium hydroxide not used by the sample is back-titrated with hydrochloric acid.

RESULTS AND DISCUSSIONS

Reaction rate curve and kinetics characteristics of carboxymethylation of starch

The reaction temperatures were set at 70, 60, 50°C, respectively. Samples were taken at different time for acid-base titration and determination of the DS. The volume of hydrochloric acid standard solution consumed by every sample V_{HCl} , the concentration of sodium hydroxide M_{NaOH} , the degree of substitution of products DS, the theoretical degree of substitution DS_{th} , and the reaction efficiency RE were shown in Tables I–III.

In these tables, ΔM_{NaOH} is the difference between the concentration of sodium hydroxide, when $t = 0$ or the reaction temperature just rises to the set temperature, and the concentration of sodium hydroxide at the reaction time t . However, there is also a change or consumption of sodium hydroxide and

TABLE II
The Experimental Data of Reaction Kinetics of Carboxymethylation of Starch (60°C)

No.	t (min)	V_{HCl} (mL)	M_{NaOH}	ΔM_{NaOH}	DS_{th}	DS	RE (%)
0			0.427				
1	0	7.4	0.371	0.056	0.0368	0.0259	
2	30	6.1	0.306	0.065	0.0421	0.0583	77.0
3	60	5.0	0.251	0.120	0.0778	0.0869	78.4
4	90	4.4	0.220	0.151	0.0978	0.1057	81.6
5	120	3.85	0.193	0.178	0.1153	0.1123	75.0
6	180	2.9	0.145	0.226	0.1464	0.1414	78.9
7	240	1.9	0.095	0.276	0.1788	0.1590	74.4

TABLE III
The Experimental Data of Reaction Kinetics of Carboxymethylation of Starch (70°C)

No.	<i>t</i> (min)	<i>V</i> _{HCl} (mL)	<i>M</i> _{NaOH}	Δ <i>M</i> _{NaOH}	DS _{th}	DS	RE
0			0.427				
1	0	6.6	0.330	0.097	0.0629	0.0499	
2	30	4.2	0.210	0.120	0.0778	0.1069	73.2
3	60	3.1	0.155	0.175	0.1134	0.1344	74.5
4	90	2.4	0.120	0.210	0.1361	0.1515	74.7
5	120	1.8	0.090	0.240	0.1556	0.1722	78.6
6	150	1.3	0.065	0.265	0.1718	0.1799	75.7
7	180	0.9	0.045	0.285	0.1847	0.1851	73.1

Note: the concentration of standard solution hydrochloric acid is 0.5010M.

chloroacetate in the period from the time soon after the addition of chloroacetic acid to the time when it is just raised to the set temperature. If defining that Δ*M*_{NaOH}⁰¹ presents the change of the concentration of sodium hydroxide in this period, then the initial concentration of chloroacetate (at *t* = 0) [C1CH2COONa]₀ and Δ*M*_{NaOH}⁰¹ have the following relationship:

$$[\text{C1CH}_2\text{COONa}]_0 = \frac{m}{M_c} \times \frac{1}{V} - \Delta M_{\text{NaOH}}^{01} \quad (9)$$

In eq. (9),

m is the total amount of chloroacetic acid added (5 g × 97%);

M_c is the molar mass, in grams per mole, of chloroacetic acid (*M_c* = 94.5g mol⁻¹);

V is the total volume of reaction system (*V* = 0.140 L, by determined);

Δ*M*_{NaOH}⁰¹ = *M*_{NaOH}⁰ - *M*_{NaOH}¹, Here the *M*_{NaOH}⁰ presents the concentration of sodium hydroxide at the time when chloroacetic acid is just added (note: not the *t* = 0, but the sample no. is 0), and the *M*_{NaOH}¹ presents the concentration of sodium hydroxide at the time *t* = 0 (the sample no. is 1).

The theoretical degree of substitution DS_{th} could be calculated as follows:

$$\text{DS}_{\text{th}} = \frac{\Delta M_{\text{NaOH}} \times V \times M_s}{W_s \times (1 - 12.5\%)} \quad (10)$$

In eq. (10),

V is the volume of reaction system (*V* = 0.14 L);

M_s is the molar mass, in grams per mole, of anhydroglucose (*M_s* = 162 g mol⁻¹);

W_s is the amount of starch added (*W_s* = 40 g);

12.5% is moisture content of the starch.

The RE was calculated from the following formula

$$\text{RE} = \frac{\text{DS} - \text{DS}_0}{\text{DS}_{\text{th}}} \times 100\% \quad (11)$$

In eq. (11),

The DS₀ is the determined result for the sample at *t* = 0, just as it rises to the set temperature.

The DS is the determined result for a sample at time *t*.

The DS_{th} is the calculated result from the Δ*M*_{NaOH} of a sample at time *t*.

According to the experimental data in the above tables and kinetics reaction rate eq. (6), reaction rate curve at each temperature was shown in Figure 1.

In Figure 1, *t* is horizontal, *y* is the vertical axis

$$y = \frac{1}{[\text{C1CH}_2\text{COONa}]_0 - [\text{NaOH}]_0} \times \ln \frac{[\text{NaOH}]_0 ([\text{C1CH}_2\text{COONa}]_0 - x)}{[\text{C1CH}_2\text{COONa}]_0 ([\text{NaOH}]_0 - x)}$$

As was shown in Figure 1, the reaction rate curves at 70, 60, 50°C are approximately beeline from the beginning to 90, 180, and 240 min, respectively. The reaction had finished nearly 80% during these periods, and the degree of substitution of the reaction products has reached to about 0.15. It can be seen that the reaction in these periods are corresponding with the character of the reaction of second-order, and the slope of the straight part is the overall

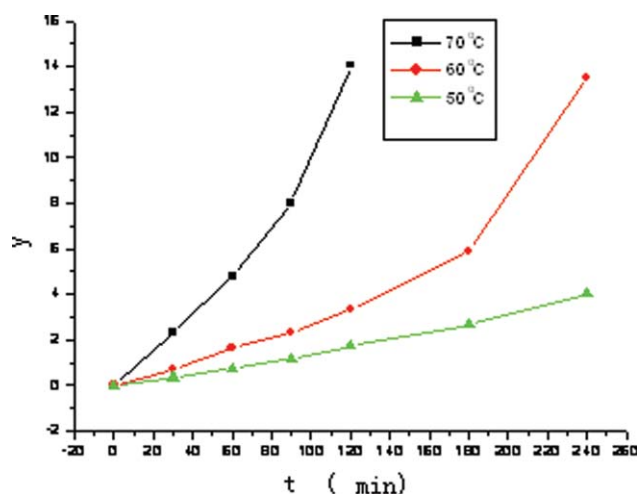


Figure 1 The reaction rate curves of carboxymethylation of starch at different temperature. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

TABLE IV
The Main and Side Reaction Rate Constants at Different Temperature

Temperature (°C)	50	60	70
The main reaction rate constant k_1 (L mol ⁻¹ min ⁻¹)	0.0138	0.0249	0.0656
The side reaction rate constant k_2 (L mol ⁻¹ min ⁻¹)	0.0029	0.0075	0.0227

reaction rate constant k (L mol⁻¹ min⁻¹) at each temperature.

Because the carboxymethylation of starch in ethanol media is multi-phase reaction, reaction has the priority to occur on the surface of starch granule in the early reaction period. However, later after the DS reached a certain value, the majority of molecules on the surface of starch granule may be carboxymethylated, and the reaction of the molecules inside starch granule was affected by the rate of the reagents diffusing into starch granule. Moreover, the carboxymethyl starch is water-soluble when the degree of substitution is near to 0.15. The starch granules swell remarkably in the reaction system. The swelling of starch granules may prevent reagents from diffusing into starch granules.^{3,7} So the later reaction shows a departure from the reaction of second-order.

A recent literature by Manal⁴ mentioned about the reaction rate of carboxymethylation of potato starch. Manal concluded that the carboxymethylation of starch was first-order reaction based on their experimental data, which is a significant difference from result in this article. Why? It is because of the different experimental methods. By Manal's experimental method, the mixture of starch and ethanol was only continuously stirred in the course of adding the solution of sodium hydroxide and sodium chloroacetate, while the stirring was stopped after the addition of the sodium chloroacetate. Then the reactive bottle was closed and kept at 30°C for a long time (50 and 168 h). As the ratio of material : liquor was 1 : 2.5, the starch must sink down to bottom of the bottle in ethanol media because of no stirring in the reaction process. Thus it is the decisive factor to control the reaction rate that the diffusion of sodium chloroacetate from the upper liquid phase to starch sunk to the bottom. This is the main reason for the different results between Manal's work and this article.

The reaction rate constants

The slope of the straight part of the three curves was obtained by linear regression analysis. The reaction rate constant k (L mol⁻¹ min⁻¹) at each temperature are:

$$k_{50} = 0.01665, k_{60} = 0.0324, k_{70} = 0.0883$$

The average of reaction efficiency under three reaction temperatures are (rounded a deviation from the maximum value):

$$RE_{50} = 82.86\%, RE_{60} = 76.88\%, RE_{70} = 74.24\%$$

Put the k values and the RE values into eqs. (7) and (8), respectively. We obtained the main and side reaction rate constants k_1 and k_2 at each temperature. The results are shown in Table IV,

Activation energy of the reaction carboxymethylation of starch

Reaction rate constant k with temperature follows the Arrhenius equation:

$$k = Ae^{-E_a/RT} \quad (12)$$

Taking the natural logarithm on both sides of the above equation, that is:

$$\ln k = -\frac{E_a}{RT} + \ln A \quad (13)$$

In the eqs. (12) and (13),

E_a is known as the Arrhenius activation energy;

R is the molar gas constant (8.31451 J K⁻¹ mol⁻¹);

T is absolute temperature;

A is called pre-exponential factor or frequency factor.

Plot curve of the $\ln k$ with $1/T$, it is a straight line. The slope is E_a/R , so activation energy E_a can be obtained.

Figures 2 and 3 are the curves of the natural logarithm of the main reaction rate constant K_1 and the side reaction rate constant K_2 with $1/T$, respectively.

Figures 2 and 3 show that the curves are good linear, indicating that the main and the side reaction rate constants obtained from experiment with

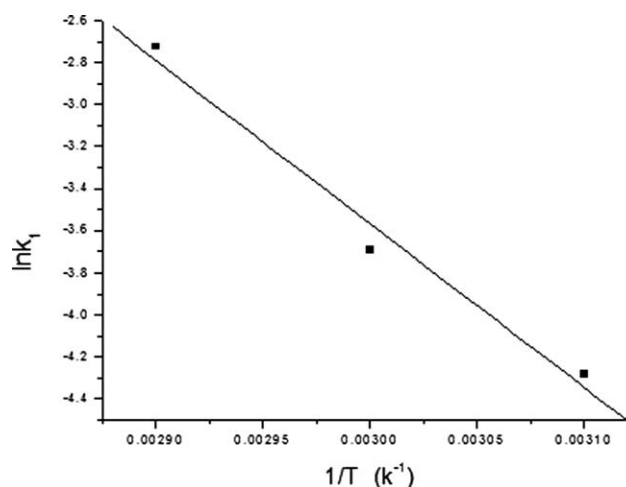


Figure 2 The relationship curve between $\ln k_1$ and $1/T$.

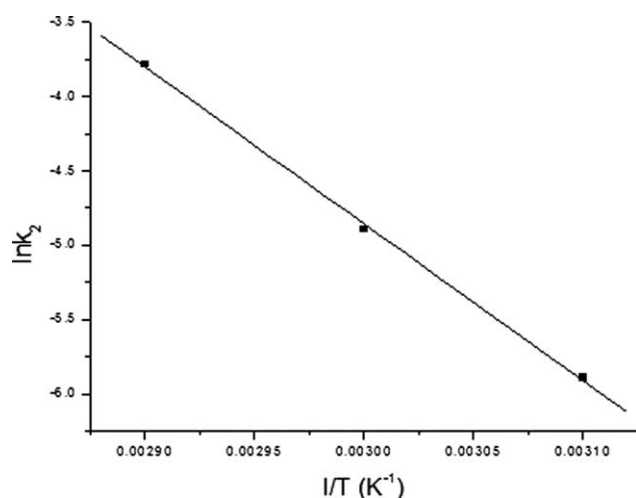


Figure 3 The relationship curve between $\ln k_2$ and $1/T$.

temperatures well follow the Arrhenius equation. Slope of the two curves are -7790 and $-10,550$ respectively, thus the reaction activation energies for the main reaction and the side reaction are: $E_1 = 64.77 \text{ kJ mol}^{-1}$, $E_2 = 87.72 \text{ kJ mol}^{-1}$. This result shows that the side reaction activation energy is higher than that of the main reaction, which is to say the higher the temperature is, the more advantages the side reaction has. Increasing the temperature, although the reaction is speeded up, however, the reaction efficiency will be reduced, which results in not only lower DS of product, but also more by-product and lower product purity.

Tijssen et al.³ had tested the effect of reaction temperature on DS and RE of carboxymethylation of potato starch in isopropyl alcohol media. After 24 h of reaction the final DS at reaction temperature of 30, 40, 50°C were all equal to 1.0 with the RE of 0.91, and then they stated that the activation energy for the main and the side reaction are equal. However, the result was different from that in this article. This maybe has something to do with the different parameters such as reaction solvent used, water ratio with solvent, and reaction temperature. First, isopropyl alcohol had been proved by many authors³⁻⁶ to be the best solvent media for carboxymethylation of starch among all the solvents such as methyl alcohol, ethyl alcohol, propyl alcohol, butyl alcohol, and etc. It showed the highest DS and RE. Second, the optimal water ratio with isopropyl alcohol was lower than that for ethyl alcohol.³⁻⁶ In the experiment of Tijssen et al., the water ratio with isopropyl alcohol was 0.1, but in this article the water ratio with ethyl alcohol was 0.16. It is clear that the effect of increasing water content to a certain extent on the DS and RE for carboxymethylation of starch will decrease the DS and RE.^{4,7} Third, the reaction temperature of Tijssen et al. is relatively low. The DS and RE of car-

boxymethylation of starch at a lower reaction temperature for a longer reaction time is higher than that at higher reaction temperature, for the chance of forming glycolate as a result of the reaction between chloroacetate and sodium hydroxide decreases, which is favored by higher temperature.^{4,7-9} As the reaction temperature of Tijssen et al. is lower, the effect of temperature on DS and RE may be relatively small. Under the multi-action of the three factors above, the difference of effect among the three temperatures on DS and RE in the experiment of Tijssen et al. might be too small to be displayed. However, the author couldn't agree with the conclusion of Tijssen et al. about the activation energies for the main and the side reactions are equal.

Moreover, Manal reported⁴ that the RE of 100% and 99.36% of carboxymethylation of potato starch at 30°C for 24 h were respectively obtained for isopropyl alcohol and ethyl alcohol media with same water ration of 90 : 10, and the RE of 86% was obtained for the ethyl alcohol with water ration of 70 : 30, but the RE became to 93% when being cooled during the addition of the agents and mixing with starch. The phenomena can further explain the effects of reaction temperature and water content on the RE of carboxymethylation of starch. However, apart from its lower reaction temperature, the lower water content, and the catalyst used, the excellent result is also likely because the DS of Manal is only 0.2, much lower than that of Tijssen et al. As the experiment of Hebeish and Khali¹⁰ proved that increasing both monochloroacetic acid and sodium hydroxide concentration was to bring about increase in DS and decrease in RE.

It can be concluded that there are many factors such as the solvent used, water content, the reaction temperature, the degree of substitute, and etc., which could affect the reaction rate, the DS, and the RE. Of course, these factors could affect the overall reaction rate constant k , the main and the side k_1 , k_2 , as well as the main and the side reaction activation energies.

CONCLUSIONS

1. The reaction kinetics of carboxymethylation of starch in early reaction stage was corresponding with the characters of the second-order reaction. It is a reaction of second-order.
2. Carboxymethylation of starch, the main and side reaction rate constants at different temperatures are consistent with Arrhenius equation. Activation energies of the main and side reaction are: $E_1 = 64.77 \text{ kJ mol}^{-1}$, $E_2 = 87.72 \text{ kJ mol}^{-1}$. The activation energy of side reaction is higher than that of the main reaction. It can be concluded that with increasing temperature,

the side reaction will increase and the efficiency of reaction will reduce.

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